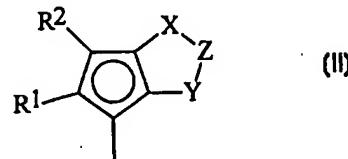




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(54) Title: METALLOCENES, LIGANDS AND OLEFIN POLYMERIZATION



(57) Abstract

A class of metallocene compounds is disclosed having the following general formula (I): $R_n(Cp)(A)ML_p$ wherein R_n is a structural bridge; Cp is a heterocyclic cyclopentadienyl group of formula (II) wherein R^1 and R^2 are hydrogen or hydrocarbon groups; M is a transition metal of group 3, 4, 5 or 6 or to the lanthanides or the actinides in the Periodic Table or the Elements (new IUPAC version); L is a monoanionic ligand; Z is NR^3 or O ; X and Y are selected from $(CR^4_2)_n$, BR^4_2 , PR^4 , SiR^4_2 or GeR^4_2 ; and substituents R^4 are hydrogen atoms or hydrocarbon radicals, with the proviso that both X and Y cannot be carbon atoms at the same time; A is a group selected from substituted or unsubstituted cyclopentadienyls, which may carry one or more condensed cycles, $=NR^5$, $-O-$, $-S-$ and $=PR^5$ groups, R^5 being defined as substituents R^1 and R^2 , and groups corresponding to formula (II); p is an integer from 0 to 3. These metallocene compounds are useful as catalyst components for the polymerization of olefins.

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METALLOCENES, LIGANDS AND OLEFIN POLYMERIZATION

FIELD OF THE INVENTION

The present invention relates to a new class of metallocene compounds, to a catalyst for the polymerization of olefins containing them and to a polymerization process carried out in the presence of said catalyst. The invention also relates to the corresponding ligands useful as intermediates in the synthesis of said metallocene compounds, as well as to processes for preparing said ligands and said metallocene compounds.

DESCRIPTION OF THE PRIOR ART

Metallocene compounds with two cyclopentadienyl groups are known as catalyst components for the polymerization of olefins.

European Patent 0 129 368, for instance, describes a catalyst system for the polymerization of olefins comprising (a) a bis-cyclopentadienyl coordination complex with a transition metal and (b) an alumoxane. The two cyclopentadienyl groups can be linked by a bridging group, which is generally a divalent radical containing one or more carbon atoms or heteroatoms.

Also known are bridged metallocene compounds wherein the cyclopentadienyl moiety is condensed to one aromatic or non aromatic ring.

For example, European Patent Application EP 0 185 918 describes the use of ethylenbis(4,5,6,7-tetrahydro-1-indenyl)zirconium dichloride together with a suitable cocatalyst for the preparation of isotactic polyolefins.

Metallocenes compounds in which the cyclopentadienyl groups have heteroatom containing substituents and catalysts containing them are also known.

From the European Patent Application EP-A2- 0 743 317 are known metallocene compounds possessing a cyclopentadienyl group containing a heteroatom as part of a substituted or condensed ring system. Illustrative examples are indenyl moieties substituted with a chinoline or pyridine radical. These catalysts containing said metallocenes are useful for the polymerization of olefins.

US Patent 5 489 659 relates to a class of silicon-containing metallocene compounds for the polymerization of alpha-olefins wherein the silicon atom is part of a non aromatic ring condensed to the cyclopentadienyl ring, such as, for example, ethylenbis(4,4-dimethyl-4,5,6,7-tetrahydro-4-silaindenyl) zirconium dichloride.

European Patent Application EP 0 590 486 describes metallocene compounds containing a cyclopentadienyl group having a heteroatom in the ring system for use in the preparation of polyolefins. The only illustrative examples are bis(1-phospha-2,3,4,5-tetramethylcyclopentadienyl) zirconium dichloride and tetrakis(2,5-dimethylpyrrol)zirconium.

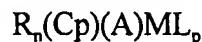
International patent application PCT/EP97/6297, in the name of the same Applicant, discloses a class of bridged and unbridged heterocyclic metallocene compounds containing a cyclopentadienyl group to which a heteroatom containing ring is fused. The catalytic system containing said metallocenes are useful for the polymerization of olefins.

It would be desirable to provide a novel class of metallocenes which, when used in catalysts for the polymerization of olefins, are suitable for the preparation of polyolefins.

SUMMARY OF THE INVENTION

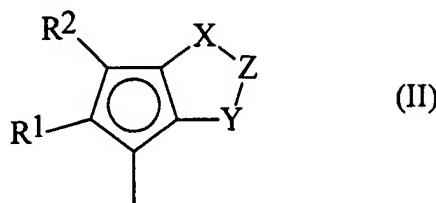
A novel class of metallocene compounds having a particular cyclopentadienyl ligand system has now unexpectedly been found, which can advantageously be used as catalyst components for the polymerization of olefins.

According to a first aspect, the present invention provides a metallocene compound of formula (I):



wherein R_n is a structural bridge;

Cp is a heterocyclic cyclopentadienyl group of formula (II):



wherein substituents R^1 and R^2 , same or different, are hydrogen atoms, C_1 - C_{20} alkyl, C_3 - C_{20} cycloalkyl, C_2 - C_{20} alkenyl, C_6 - C_{20} aryl, C_7 - C_{20} alkylaryl, or C_7 - C_{20} arylalkyl radicals, optionally two adjacent substituents R^1 and R^2 can form a cycle comprising from 5 to 8 carbon atoms and, furthermore, substituents R^1 and R^2 can contain silicon or germanium atoms;

Z is NR^3 or O , R^3 being defined as substituents R^1 and R^2 ;

X and Y , same or different, are selected from $(CR^4_2)_r$, BR^4_2 , PR^4 , SiR^4_2 or GeR^4_2 ; and substituents R^4 , same or different, are hydrogen atoms, C_1 - C_{20} alkyl, C_3 - C_{20} cycloalkyl, C_2 - C_{20} alkenyl, C_6 - C_{20} aryl, C_7 - C_{20} alkylaryl or C_7 - C_{20} arylalkyl radicals; and, furthermore, substituents R^4 can contain hetero atoms such as nitrogen, phosphor, oxygen, silicon or germanium atoms, with the proviso that both X and Y can not be carbon atoms at the same time;

A is a group selected from substituted or unsubstituted cyclopentadienyls, which may carry one or more condensed cycles, $=NR^5$, $-O-$, $-S-$ and $=PR^5$ groups, R^5 being defined as substituents R^1 and R^2 , and groups corresponding to formula (II);

M is a transition metal selected from those belonging to group 3, 4, 5 or 6 or to the lanthanides or the actinides of the Periodic Table of the Elements (new IUPAC version);

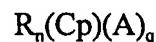
the substituent L, same or different, is a monoanionic ligand, selected from the group consisting of hydrogen, halogen, $-SR^6$, R^6 , $-OR^6$, $-NR^6_2$, $OCOR^6$, OSO_2CF_3 and PR^6_2 , wherein the substituents R^6 , same or different, are linear or branched, saturated or unsaturated C_1-C_{20} alkyl, C_3-C_{20} cycloalkyl, C_2-C_{20} alkenyl, C_6-C_{20} aryl, C_7-C_{20} alkylaryl, or C_7-C_{20} arylalkyl radicals, optionally containing silicon or germanium atoms;

p is an integer from 0 to 3, p being equal to the oxidation state of the metal M minus two;

n is an integer ranging from 0 to 4; and

r is an integer ranging from 1 to 4.

According to another aspect of the present invention there is provided a new class of ligands of formula (III):



wherein R, n, Cp, A, have the meanings as reported above and q is 0 when n is 0 and is 1 when n is 1 to 4, particularly useful as intermediates in the preparation of the metallocene compounds of formula (I).

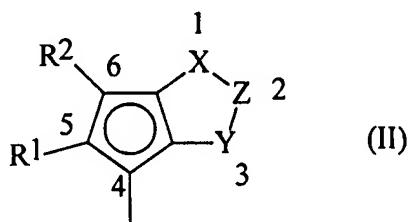
A further aspect of the present invention is a process for the preparation of ligands $R_n(Cp)(A)_q$ of formula (III), wherein R, n, Cp, A and q have the meanings as reported above.

A still further aspect of the present invention is a process for the preparation of the metallocene compounds of formula (I), obtainable by contacting the ligand of formula (III) $R_n(Cp)(A)_q$ with a compound of formula ML_{p+2} , wherein M, L and p are defined as above, in the presence of a compound capable of forming the corresponding dianionic compound of the ligand of formula (III).

Another aspect of the present invention is a catalyst for the polymerization of olefins comprising said heterocyclic metallocene and the use thereof in the polymerization of olefins.

DETAILED DESCRIPTION OF THE INVENTION

The numbering of the substituents on the cyclopentadienyl group of formula (II), to which reference is made in the present invention, is the following:



In the metallocene compounds of the aforementioned type, the cyclopentadienyl group of formula (II) may be linked to an identical cyclopentadienyl group, to a cyclopentadienyl derivate or to a heteroatom containing group, such as an amino group, by divalent radicals containing one or more carbon atoms, such as CH_2 groups, or atoms other than carbon atoms, such as dimethylsilanediyl groups, linking the cyclopentadienyl group in the 4 position of the above ring system to either an identical cyclopentadienyl group, to a cyclopentadienyl derivate or to a heteroatom containing group.

An advantageous class of heterocyclic metallocenes according to the present invention corresponds to formula (I) wherein A is a group selected from substituted or unsubstituted cyclopentadienyls, which may carry one or more aromatic or non-aromatic condensed cycles, such as indenyl, fluorenyl, benzoindenyl, hydrogenated or partially hydrogenated cycles, and n is different from 0, i.e. the two cyclopentadienyl groups are linked to each other by a bridging divalent group. Preferably, the divalent group $(\text{QR}^7)_n$ is selected from the group consisting of CR^7_2 , SiR^7_2 , GeR^7_2 , NR^7 , PR^7 and $(\text{CR}^7_2)_2$ and the R^7 groups, equal or different, are linear or

branched, saturated or unsaturated C₁-C₂₀ alkyl, C₃-C₂₀ cycloalkyl, C₂-C₂₀ alkenyl, C₆-C₂₀ aryl, C₇-C₂₀ alkylaryl, or C₇-C₂₀ arylalkyl radicals optionally, when Q is C, Si or Ge, both substituents R⁷ can form a cycle comprising from 3 to 8 atoms. More preferably, said divalent bridge is Si(CH₃)₂, SiPh₂, CH₂, (CH₂)₂ or C(CH₃)₂.

m is 1 or 2, being 1 when Q is N or P, and being 2 when Q is C, Si or Ge; n ranges from 0 to 6 and, when n > 1, the atoms Q can be the same or different, such as, for example, in the bridges -CH₂-Si(CH₃)₂-², -CH₂-NR²- and CH₂-PR²-.

The transition metal is preferably titanium, zirconium and hafnium, more preferably it is zirconium.

The substituents R¹ and R² are preferably hydrogen atoms.

The substituents L are preferably halogen atoms or R⁶ groups, R⁶ being defined as reported above. More preferably they are chlorine atoms or methyl groups.

A more advantageous class of heterocyclic metallocenes according to the present invention corresponds to formula (I) wherein A is represented by the above formula (II), i.e., the two cyclopentadienyl moieties of the metallocene compound of the invention are identical.

Non limitative examples of said metallocenes are:

isopropylidenebis{2-(methyl)-1,1,3,3-tetramethyl-1,2,3,3a-tetrahydrocyclopenta[c][1,2,5]azadisilole}zirconium dichloride or dimethyl;

isopropylidenebis{2-(ethyl)-1,1,3,3-tetramethyl-1,2,3,3a-tetrahydrocyclopenta[c][1,2,5]azadisilole}zirconium dichloride or dimethyl;

isopropylidenebis{2-(iso-propyl)-1,1,3,3-tetramethyl-1,2,3,3a-tetrahydrocyclopenta[c][1,2,5]azadisilole}zirconium dichloride or dimethyl;

isopropylidenebis{2-(tert-butyl)-1,1,3,3,5-pentamethyl-1,2,3,3a-tetrahydrocyclopenta[c][1,2,5]azadisilole}zirconium dichloride or dimethyl;

isopropylidenebis{2-(ethyl)-1,1,3,3,5-pentamethyl-1,2,3,3a-tetrahydrocyclopenta[c][1,2,5]azadisilole}zirconium dichloride or dimethyl;

isopropylidenebis{2-(iso-propyl)-1,1,3,3,5-pentamethyl-1,2,3,3a-tetrahydrocyclopenta[c][1,2,5]azadisilole}zirconium dichloride or dimethyl;

isopropylidenebis{2-(tert-butyl)-1,1,3-trimethyl-1,2,3,3a-tetrahydrocyclopenta[c][1,2,5]azaborasilole}zirconium dichloride or dimethyl;

isopropylidenebis{2-(tert-butyl)-1,1,3-trimethyl-1,2,3,3a-tetrahydrocyclopenta[c][1,2,5]azaphosphasilole}zirconium dichloride or dimethyl;

isopropylidenebis{2-(tert-butyl)-1,3-dimethyl-1,2,3,3a-tetrahydrocyclopenta[c][1,2,5]azadiborole}zirconium dichloride or dimethyl;

isopropylidenebis{2-(tert-butyl)-1,3-dimethyl-1,2,3,3a-tetrahydrocyclopenta[c][1,2,5]azadiphosphole}zirconium dichloride or dimethyl;

isopropylidenebis{2-(tert-butyl)-1,1,3,5-tetramethyl-1,2,3,3a-tetrahydrocyclopenta[c][1,2,5]azaborasilole}zirconium dichloride or dimethyl;

isopropylidenebis{2-(tert-butyl)-1,1,3,5-tetramethyl-1,2,3,3a-tetrahydrocyclopenta[c][1,2,5]azaphosphasilole}zirconium dichloride or dimethyl;

isopropylidenebis{2-(tert-butyl)-1,3,5-trimethyl-1,2,3,3a-tetrahydrocyclopenta[c][1,2,5]azadiborole}zirconium dichloride or dimethyl;

isopropylidenebis{2-(tert-butyl)-1,3,5-trimethyl-1,2,3,3a-tetrahydrocyclopenta[c][1,2,5]azadiphosphole}zirconium dichloride or dimethyl;

dimethylsilanediylbis{2-(tert-butyl)-1,1,3-trimethyl-1,2,3,3a-tetrahydrocyclopenta[c][1,2,5]

azaborasilole}zirconium dichloride or dimethyl;

dimethylsilanediylbis{2-(tert-butyl)-1,1,3-trimethyl-1,2,3,3a-tetrahydrocyclopenta[c][1,2,5]

azaphosphasilole}zirconium dichloride or dimethyl;

dimethylsilanediylbis{2-(tert-butyl)-1,3-dimethyl-1,2,3,3a-tetrahydrocyclopenta[c][1,2,5]

azadiborole}zirconium dichloride or dimethyl;

dimethylsilanediylbis{2-(tert-butyl)-1,3-dimethyl-1,2,3,3a-tetrahydrocyclopenta[c][1,2,5]

azadiphosphole}zirconium dichloride or dimethyl;

dimethylsilanediylbis{2-(tert-butyl)-1,3,5-trimethyl-1,2,3,3a-tetrahydrocyclopenta[c][1,2,5]

azadiborole}zirconium dichloride or dimethyl;

dimethylsilanediylbis{2-(tert-butyl)-1,3,5-trimethyl-1,2,3,3a-tetrahydrocyclopenta[c][1,2,5]

azadiphosphole}zirconium dichloride or dimethyl;

ispropylidene{2-(tert-butyl)-1,1-dimethyl-2,3,4,7a-tetrahydro-1H-cyclopenta[c][1,2]

azasiline}zirconium dichloride or dimethyl;

dimethylsilanediylbis{2-(tert-butyl)-1,1-dimethyl-2,3,4,7a-tetrahydro-1H-cyclopenta[c][1,2]

azasiline}zirconium dichloride or dimethyl;

Another interesting class of heterocyclic metallocenes according to the present invention corresponds to formula (I), wherein A corresponds to formula (II) and n = 0, i.e., the two identical cyclopentadienyl groups are not linked to each other by a bridging divalent group.

Non limiting examples of said class are:

{2-(tert-butyl)-1,1,3,3-tetramethyl-1,2,3,3a-tetrahydrocyclopenta[c][1,2,5]

azadisilole}zirconium dichloride or dimethyl;

{2-(tert-butyl)-1,1,3,3,5-pentamethyl-1,2,3,3a-tetrahydrocyclopenta[c][1,2,5]azadisilole}

zirconium dichloride or dimethyl;

{2-(methyl)-1,1,3,3-tetramethyl-1,2,3,3a-tetrahydrocyclopenta [c][1,2,5] azadisilole}zirconium dichloride or dimethyl;

{2-(methyl)-1,1,3,3,5-pentamethyl-1,2,3,3a-tetrahydrocyclopenta[c][1,2,5]
azadisilole}zirconium dichloride or dimethyl;

{2-(ethyl)-1,1,3,3-tetramethyl-1,2,3,3a-tetrahydrocyclopenta[c][1,2,5]azadisilole}zirconium dichloride or dimethyl;

{2-(ethyl)-1,1,3,3,5-pentamethyl-1,2,3,3a-tetrahydrocyclopenta [c] [1,2,5]
azadisilole}zirconium dichloride or dimethyl;

{2-(iso-propyl)-1,1,3,3-tetramethyl-1,2,3,3a-tetrahydrocyclopenta[c][1,2,5]azadisilole}
zirconium dichloride or dimethyl;

{2-(iso-propyl)-1,1,3,3,5-pentamethyl-1,2,3,3a-tetrahydrocyclopenta[c][1,2,5]azadisilole}
zirconium dichloride or dimethyl;

{2-(tert-butyl)-1,1,3-trimethyl-1,2,3,3a-tetrahydrocyclopenta [c] [1,2,5]
azaborasilole}zirconium dichloride or dimethyl;

{2-(tert-butyl)-1,1,3-trimethyl-1,2,3,3a-tetrahydrocyclopenta[c][1,2,5]azaphosphasilole}
zirconium dichloride or dimethyl;

{2-(tert-butyl)-1,3-dimethyl-1,2,3,3a-tetrahydrocyclopenta[c][1,2,5]azadiborol}zirconium dichloride or dimethyl;

{2-(tert-butyl)-1,3-dimethyl-1,2,3,3a-tetrahydrocyclopenta [c][1,2,5]
azadiphosphole}zirconium dichloride or dimethyl;

{2-(tert-butyl)-1,1,3,5-tetramethyl-1,2,3,3a-tetrahydrocyclopenta[c][1,2,5]azaborasilole}

zirconium dichloride or dimethyl;

{2-(tert-butyl)-1,1,3,5-tetramethyl-1,2,3,3a-tetrahydrocyclopenta[c][1,2,5]azaphosphasilole}

zirconium dichloride or dimethyl;

{2-(tert-butyl)-1,3,5-trimethyl-1,2,3,3a-tetrahydrocyclopenta[c][1,2,5]azadiborol}zirconium dichloride or dimethyl;

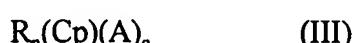
{2-(tert-butyl)-1,3,5-trimethyl-1,2,3,3a-

tetrahydrocyclopenta[c][1,2,5]azadiphosphole}zirconium dichloride or dimethyl;

{2-(tert-butyl)-1,1-dimethyl-2,3,4,7a-tetrahydro-1H-cyclopenta[c][1,2]azasiline}zirconium dichloride or dimethyl;

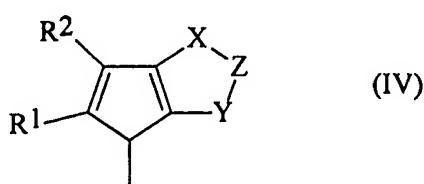
{2-(tert-butyl)-1,1-dimethyl-2,3,4,7a-tetrahydro-1H-cyclopenta[c][1,2]azasiline}zirconium dichloride or dimethyl;

According to another aspect of the present invention there is provided a class of ligands of formula (III):



wherein R_n is a structural bridge;

Cp is a heterocyclic cyclopentadienyl group of formula (IV):



wherein R , R^1 , R^2 , X , Y and Z , n and q have the meaning as reported, A is a group selected from substituted or unsubstituted cyclopentadienyls, which may carry one or more condensed

cycles, =NR⁵, -O-, -S- and =PR⁵ groups, R⁵ being defined as substituents R¹ and R², and groups corresponding to formula (IV).

The two double bonds of the cyclopentadienyl ring of the ligands of formula (IV) can be in any of the allowed positions.

The aforementioned compounds of formula (IV) are particularly useful as intermediate ligands for the preparation of the heterocyclic metallocene compounds of formula (I).

An advantageous class of heterocyclic ligands according to the present invention corresponds to formula (III) wherein A is a group selected from substituted or unsubstituted cyclopentadienyls, which may carry one or more aromatic or non-aromatic condensed cycles, such as indenyl, fluorenyl, benzoindenyl, hydrogenated or partially hydrogenated cycles, and n is different from 0, i.e. the two cyclopentadienyl moieties are linked to each other by a bridging divalent radical. As to the divalent group R_n, reference is made to the above said.

A more advantageous class of heterocyclic ligands according to the present invention corresponds to formula (III) wherein n is different from 0 and A corresponds to formula (IV).

Non-limiting examples of this class of ligands according to the invention are:

isopropylidenebis{2-(tert-butyl)-1,1,3,3-tetramethyl-1,2,3,3a-tetrahydrocyclopenta[c][1,2,5]azadisilole};

isopropylidenebis{2-(methyl)-1,1,3,3-tetramethyl-1,2,3,3a-tetrahydrocyclopenta[c][1,2,5]azadisilole};

isopropylidenebis{2-(ethyl)-1,1,3,3-tetramethyl-1,2,3,3a-tetrahydrocyclopenta[c][1,2,5]azadisilole};

isopropylidenebis{2-(iso-propyl)-1,1,3,3-tetramethyl-1,2,3,3a-tetrahydrocyclopenta[c][1,2,5]azadisilole};

isopropylidene{2-(tert-butyl)-1,1,3,3,5-pentamethyl-1,2,3,3a-tetrahydrocyclopenta[c][1,2,5]azadisilole};
isopropylidene{2-(ethyl)-1,1,3,3,5-pentamethyl-1,2,3,3a-tetrahydrocyclopenta[c][1,2,5]azadisilole};
isopropylidene{2-(iso-propyl)-1,1,3,3,5-pentamethyl-1,2,3,3a-tetrahydrocyclopenta[c][1,2,5]azadisilole};
isopropylidenebis{2-(tert-butyl)-1,1,3-trimethyl-1,2,3,3a-tetrahydrocyclopenta[c][1,2,5]azaborasilole};
isopropylidenebis{2-(tert-butyl)-1,1,3-trimethyl-1,2,3,3a-tetrahydrocyclopenta[c][1,2,5]azaphosphasilole};
isopropylidenebis{2-(tert-butyl)-1,3-dimethyl-1,2,3,3a-tetrahydrocyclopenta[c][1,2,5]azadiborol};
isopropylidenebis{2-(tert-butyl)-1,3-dimethyl-1,2,3,3a-tetrahydrocyclopenta[c][1,2,5]azadiphosphole};
isopropylidenebis{2-(tert-butyl)-1,1,3,5-tetramethyl-1,2,3,3a-tetrahydrocyclopenta[c][1,2,5]azaborasilole};
isopropylidenebis{2-(tert-butyl)-1,1,3,5-tetramethyl-1,2,3,3a-tetrahydrocyclopenta[c][1,2,5]azaphosphasilole};
isopropylidenebis{2-(tert-butyl)-1,3,5-trimethyl-1,2,3,3a-tetrahydrocyclopenta[c][1,2,5]azadiborol};
isopropylidenebis{2-(tert-butyl)-1,3,5-trimethyl-1,2,3,3a-tetrahydrocyclopenta[c][1,2,5]azadiphosphole};

dimethylsilanediylbis{2-(tert-butyl)-1,1,3-trimethyl-1,2,3,3a-tetrahydrocyclopenta[c][1,2,5]azaborasilole};

dimethylsilanediylbis{2-(tert-butyl)-1,1,3-trimethyl-1,2,3,3a-tetrahydrocyclopenta[c][1,2,5]azaphosphasilole};

dimethylsilanediylbis{2-(tert-butyl)-1,3-dimethyl-1,2,3,3a-tetrahydrocyclopenta[c][1,2,5]azadiborol};

dimethylsilanediylbis{2-(tert-butyl)-1,3-dimethyl-1,2,3,3a-tetrahydrocyclopenta[c][1,2,5]azadiphosphole};

dimethylsilanediylbis{2-(tert-butyl)-1,1,3,5-tetramethyl-1,2,3,3a-tetrahydrocyclopenta[c][1,2,5]azaborasilole};

dimethylsilanediylbis{2-(tert-butyl)-1,1,3,5-tetramethyl-1,2,3,3a-tetrahydrocyclopenta[c][1,2,5]azaphosphasilole};

dimethylsilanediylbis{2-(tert-butyl)-1,3,5-trimethyl-1,2,3,3a-tetrahydrocyclopenta[c][1,2,5]azadiborol};

dimethylsilanediylbis{2-(tert-butyl)-1,3,5-trimethyl-1,2,3,3a-tetrahydrocyclopenta[c][1,2,5]azadiphosphole};

isopropylidenebis{2-(tert-butyl)-1,1-dimethyl-2,3,4,7a-tetrahydro-1H-cyclopenta[c][1,2]azasiline};

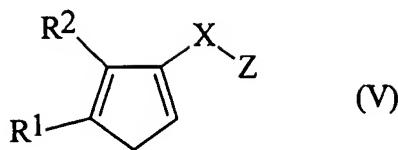
dimethylsilanediylbis{2-(tert-butyl)-1,1-dimethyl-2,3,4,7a-tetrahydro-1H-cyclopenta[c][1,2]azasiline}.

A further interesting class of ligands according to the present invention corresponds to formula (III), wherein A corresponds to formula (IV) and n = 0, i.e., the two identical cyclopentadienyl groups are not linked to each other by a bridging divalent residue.

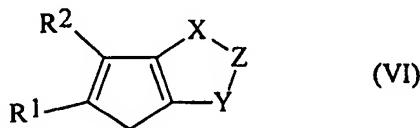
Non limiting examples of said ligands are:

bis{2-(tert-butyl)-1,1,3,3-tetramethyl-1,2,3,3a-tetrahydrocyclopenta[c] [1,2,5] azadisilole};
bis{2-(tert-butyl)-1,1,3,3,5-pentamethyl-1,2,3,3a- tetrahydrocyclopenta[c] [1,2,5] azadisilole};
bis{2-(methyl)-1,1,3,3-tetramethyl-1,2,3,3a-tetrahydrocyclopenta [c] [1,2,5] azadisilole};
bis{2-(methyl)-1,1,3,3,5-pentamethyl-1,2,3,3a-tetrahydrocyclopenta [c] [1,2,5] azadisilole};
bis{2-(ethyl)-1,1,3,3-tetramethyl-1,2,3,3a-tetrahydrocyclopenta [c] [1,2,5] azadisilole};
bis{2-(ethyl)-1,1,3,3,5-pentamethyl-1,2,3,3a-tetrahydrocyclopenta [c] [1,2,5] azadisilole};
bis{2-(iso-propyl)-1,1,3,3-tetramethyl-1,2,3,3a- tetrahydrocyclopenta[c] [1,2,5] azadisilole};
bis{2-(iso-propyl)-1,1,3,3,5-pentamethyl-1,2,3,3a-tetrahydrocyclopenta[c][1,2,5] azadisilole};
bis{2-(tert-butyl)-1,1,3-trimethyl-1,2,3,3a-tetrahydrocyclopenta [c] [1,2,5] azaborasilole};
bis{2-(tert-butyl)-1,1,3-trimethyl-1,2,3,3a-tetrahydrocyclopenta [c] [1,2,5] azaphosphasilole};
bis{2-(tert-butyl)-1,3-dimethyl-1,2,3,3a-tetrahydrocyclopenta [c] [1,2,5] azadiborol};
bis{2-(tert-butyl)-1,3-dimethyl-1,2,3,3a-tetrahydrocyclopenta [c] [1,2,5] azadiphosphole};
bis{2-(tert-butyl)-1,1,3,5-tetramethyl-1,2,3,3a-tetrahydrocyclopenta[c] [1,2,5] azaborasilole}
bis{2-(tert-butyl)-1,1,3,5-tetramethyl-1,2,3,3a-tetrahydrocyclopenta[c][1,2,5]
azaphosphasilole};
bis{2-(tert-butyl)-1,3,5-trimethyl-1,2,3,3a-tetrahydrocyclopenta [c] [1,2,5] azadiborol};
bis{2-(tert-butyl)-1,3,5-trimethyl-1,2,3,3a-tetrahydrocyclopenta [c] [1,2,5] azadiphosphole}.

According to a further aspect of the present invention there is provided a process for the preparation of ligands $R_n(Cp)(A)_q$ of formula (III), wherein R has the meaning as described above, Cp corresponds to formula (IV), A has the meaning as reported above and both n and q are 0, comprising the step of contacting a compound of formula (V):



and its double bond isomers, wherein X, R¹ and R² are defined as above and Z is nitrogen, with a compound of general formula YZ',₂ wherein Y is defined as above and Z' is a halogen atom, in the presence of a base, to form a compound of formula (VI)

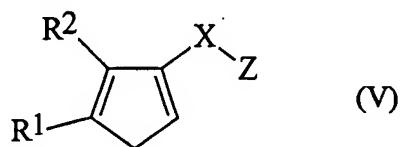


and its double bond isomers.

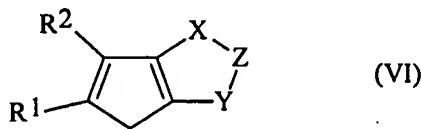
The aforementioned cyclopentadienyl derivate of formula (V) can be prepared by means of known methods such as those as described in International Patent Application PCT/US92/08730.

According to a still further aspect of the present invention there is provided a process for the preparation of a ligand R_n(Cp)(A')_q of formula (IIIa), wherein R has the meaning as reported above, n is an integer from 1 to 4 and q is 1, i.e. the two groups Cp and A' are linked by a divalent bridge, A' is a group selected from substituted or unsubstituted cyclopentadienyls, which may carry one or more condensed cycles, =NR⁵, -O-, -S- and =PR⁵ groups, R⁵ being defined as substituents R¹ and R², Cp corresponds to formula (IV) and Z' is a halogen atom, comprising the following steps:

(a) contacting a compound of formula (V):

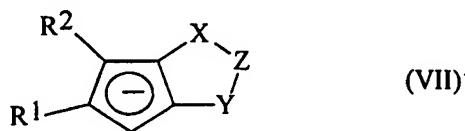


and its double bond isomers, wherein X, R¹ and R² have the meaning as reported above and Z is nitrogen, with a compound of general formula YZ'₂, wherein Y and Z' are defined above, in the presence of a base, to form a compound of formula (VI)



and its double bond isomers, and

(b) contacting with a compound able to form an anion of formula (VII)



and thereafter with a compound of general formula (VIII)



in a molar ratio (VII)/(VIII) equal to or higher than 2, or with a compound of general formula (IX)



in a molar ratio (VII)/(IX) equal to or greater than 1.

As to the structural bridge R_n in the above ligands, reference is made to the above said.

Non-limiting examples of bases used to form the above compounds of formula (VI) are hydroxides and hydrides of alkali or earth-alkali metals, metallic sodium or potassium and organometallic lithium compounds. Preferably, methyl lithium or n-butyllithium is used.

Non-limiting examples of compounds able to form the anionic compounds of formula (VII) are hydroxides and hydrides of alkali or earth-alkali metals, metallic sodium or potassium and organometallic lithium compounds. Preferably, methyl lithium or n-butyllithium is used.

Non-limiting examples of compounds of general formula $R_nZ'_2$ (VIII) are dimethyldichlorosilane, diphenyldichlorosilane, dimethyldichlorogermanium, 2,2-dichloropropane and 1,2-dibromoethane.

The synthesis of the above bridged ligands is preferably carried out by adding a solution of an organic lithium compound in an apolar solvent to a solution of the compound (VI) in an aprotic polar solvent. The thus obtained solution containing the compound (VII) in the anionic form is then added to a solution of the compound of formula $R_nZ'_2$ in an aprotic polar solvent. The bridged ligand can be finally separated by conventional general known procedures.

Not limitative examples of aprotic polar solvents which can be used in the above process are tetrahydrofuran, dimethoxyethane, diethylether, toluene and dichloromethane. Not limitative examples of apolar solvents suitable for the above process are pentane, hexane and benzene.

During the whole process, the temperature is preferably kept between -180°C and 80°C, and more preferably between -20°C and 40°C.

A still further aspect of the present invention is a process for the preparation of the metallocene compounds of formula (I), obtainable by contacting the ligand $R_n(Cp)(A)_q$ of formula (III) as described above, with a compound capable of forming a corresponding dianionic compound thereof and thereafter with a compound of formula ML_{p+2} , wherein M, L and p have the meanings as defined above.

The compound able to form said dianion is selected from the group consisting of hydroxides and hydrides of alkali- and earth-alkali metals, metallic sodium and potassium, and organometallic lithium salts, and preferably said anion is n-butyllithium.

Non-limiting examples of compounds of formula ML_{p+2}^1 are titanium tetrachloride, zirconium tetrachloride and hafnium tetrachloride.

The metallocene compounds of formula (I), when n is different from 0 and A is a cyclopentadienyl derivate, can be prepared by first reacting the bridged ligands of formula (III), prepared as described above, with a compound able to form a delocalized anion on the cyclopentadienyl rings, and thereafter with a compound of formula ML_{p+2} , wherein M and the substituents L are defined as above. Non limitative examples of compounds of formula ML_{p+2} are titanium tetrachloride, zirconium tetrachloride and hafnium tetrachloride.

More specifically, said bridged ligands are dissolved in an aprotic polar solvent and to the obtained solution is added a solution of an organic lithium compound in an apolar solvent. The thus obtained anionic form is separated, dissolved in an aprotic polar solvent and thereafter added to a suspension of the compound ML_{p+2} in an aprotic polar solvent. At the end of the reaction, the solid product obtained is separated from the reaction mixture by techniques commonly used in the state of the art. Non limitating examples of aprotic polar solvents suitable for the above reported processes are tetrahydrofuran, dimethoxyethane, diethylether, toluene and dichloromethane. Non limitating examples of apolar solvents suitable for the above process are pentane, hexane and benzene.

During the whole process, the temperature is preferably kept between -180°C and 80°C, and more preferably between -20°C and 40°C.

The unbridged metallocene compounds of formula (I), wherein n = 0 and A corresponds to formula (II), can be prepared by reacting the anions of the formula (VII) with a tetrahalide of the transition metal M (i.e. ML_4), M and L having the above described meanings, said reaction being carried out in a suitable solvent.

When at least one L substituent in the metallocene compound of formula (I) is different from halogen, it is necessary to substitute at least one substituent L in the obtained metallocene with

at least another substituent different from halogen. Such a substitution reaction is carried out by methods known in the state of the art. For example, when the substituents L are alkyl groups, the metallocenes can be reacted with alkylmagnesium halides (Grignard reagents) or with lithiumalkyl compounds.

During the whole process, the temperature is preferably kept between -180°C and 80°C, and more preferably between -20°C and 40°C.

The heterocyclic metallocene compounds of the present invention can conveniently be used as catalyst components for the polymerization of olefins.

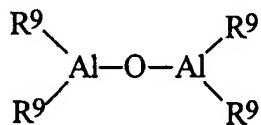
Thus, according to a still further aspect of the present invention there is provided a catalyst for the polymerization of olefins, obtainable by contacting:

- (A) a metallocene compound of formula (I), and
- (B) an alumoxane and/or a compound capable of forming an alkyl metallocene cation.

The alumoxane used as component (B) can be obtained by reacting water with an organo-aluminium compound of formula AlR^8_3 , or $Al_2R^8_6$, where at least one R^8 is not halogen. In this reaction the molar ratio of Al/water is comprised between 1:1 and 100:1.

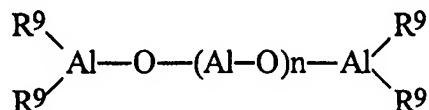
The molar ratio between aluminium and the metal of the metallocene is comprised between about 10:1 and about 20000:1, and preferably between about 100:1 and about 5000:1.

The alumoxanes used in the catalyst according to the invention are considered to be linear, branched or cyclic compounds containing at least one group of the type:

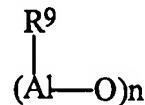


wherein the R⁹ substituents, same or different, are hydrogen atoms, C₁-C₂₀-alkyl, C₃-C₂₀-cyclalkyl, C₆-C₂₀-aryl, C₇-C₂₀-alkylaryl or C₇-C₂₀-arylalkyl, optionally containing silicon or germanium atoms, or are a -O-Al(R⁹)₂ group and, if appropriate, some R⁹ substituents can be halogen atoms.

In particular, alumoxanes of the formula:



can be used in the case of linear compounds, wherein n is 0 or an integer from 1 to 40 and the R⁹ substituents are defined as above, or alumoxanes of the formula:



can be used in the case of cyclic compounds, wherein n is an integer from 2 to 40 and the R⁹ substituents are defined as above.

Examples of alumoxanes suitable for use according to the present invention are methylalumoxane (MAO), isobutylalumoxane (TIBAO) and 2,4,4-trimethyl-pentylalumoxane (TIOAO).

In the catalyst used in the process according to the invention for the preparation of polyolefins, both the heterocyclic metallocene compound of the formula (I) and the alumoxane can be present as the product of the reaction with an organometallic aluminium compound of the formula AlR⁸₃ or Al₂R⁸₆, in which the R⁸ substituents, same or different, are hydrogen atoms, halogen atoms, C₁-C₂₀-alkyl, C₃-C₂₀-cyclalkyl, C₆-C₂₀-aryl, C₇-C₂₀-alkylaryl or C₇-C₂₀-arylalkyl, optionally containing silicon or germanium atoms.

Non-limiting examples of aluminium compounds of the formula AlR_3 , or Al_2R_6 are: $\text{Al}(\text{Me})_3$, $\text{Al}(\text{Et})_3$, $\text{AlH}(\text{Et})_2$, $\text{Al}(\text{iBu})_3$, $\text{Al}(\text{iHex})_3$, $\text{Al}(\text{iOct})_3$, $\text{Al}(\text{C}_6\text{H}_5)_3$, $\text{Al}(\text{CH}_2\text{C}_6\text{H}_5)_3$, $\text{Al}(\text{CH}_2\text{CMe}_3)_3$, $\text{Al}(\text{CH}_2\text{SiMe}_3)_3$, $\text{Al}(\text{Me})_2\text{iBu}$, $\text{Al}(\text{Me})_2\text{Et}$, $\text{AlMe}(\text{Et})_2$, $\text{AlMe}(\text{iBu})_2$, $\text{Al}(\text{Me})_2\text{iBu}$, $\text{Al}(\text{Me})_2\text{Cl}$, $\text{Al}(\text{Et})_2\text{Cl}$, AlEtCl_2 , $\text{Al}_2(\text{Et})_3\text{Cl}_3$, wherein Me=methyl, Et=ethyl, iBu=isobutyl, iHex=isoheptyl, iOct=2,4,4-trimethyl-pentyl.

Among the aforementioned aluminium compounds, trimethylaluminium (TMA), triisobutylaluminium (TIBAL) and tris(2,4,4-trimethyl-pentyl)aluminium (TIOA) are preferred.

Non limitative examples of compounds able to form a metallocene alkyl cation are compounds of formula T^+D^- , wherein T^+ is a Broensted acid, able to give a proton and to react irreversibly with a substituent L of the metallocene of formula (I), and D^- is a compatible anion, which does not coordinate, which is able to stabilize the active catalytic species which originates from the reaction of the two compounds and which is sufficiently labile to be able to be removed from an olefinic substrate. Preferably, the anion D^- comprises one or more boron atoms. More preferably, the anion D^- is an anion of the formula $\text{BAr}^{(-)}_4$, wherein substituents Ar, the same or different from each other, are aryl radicals such as phenyl, pentafluorophenyl, bis(trifluoromethyl)phenyl. Particularly preferred is the tetrakis-pentafluorophenyl borate. Furthermore, compounds of formula BAr_3 can be suitably used.

The catalysts used in the process of the present invention can be also used on inert supports. This is obtained by depositing the metallocene (A), or the product of the reaction of the same with the component (B), or the component (B) and thereafter the metallocene (A), on supports such as for example silica, alumina, styrene-divinylbenzene copolymers, polyethylene or polypropylene.

The solid compound so obtained, in combination with further addition of the alkyl aluminium compound as such or pre-reacted with water, is usefully employed in gas phase polymerisation. Catalysts of the present invention are useful in the homo- and copolymerization reaction of olefins.

Therefore, a still further object of the present invention is a process for the polymerization of olefins comprising the polymerization reaction of at least an olefinic monomer in the presence of a catalyst as above described.

The catalysts of the present invention can be used in the homo-polymerisation reaction of olefins, preferably of ethylene for the preparation of HDPE, or of α -olefins, such as propylene and 1-butene. In ethylene polymerisation, the heterocyclic metallocenes of the invention show good activities even when used in very low Al/Zr ratios.

Another interesting use of the catalysts according to the present invention is in the copolymerization of ethylene with higher olefins. In particular, the catalysts of the invention can be used for the preparation of LLDPE.

Suitable olefins to be used as comonomers comprise α -olefins of the formula $\text{CH}_2=\text{CHR}^{10}$, wherein R^{10} is an alkyl radical having from 1 to 10 carbon atoms, and cycloolefins. Examples of these olefins are propylene, 1-butene, 1-pentene, 4-methyl-1-pentene, 1-hexene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-eicosene, allylcyclohexene, cyclopentene, cyclohexene, norbornene and 4,6-dimethyl-1-heptene.

The copolymers may also contain small proportions of units deriving from polyenes, in particular from straight or cyclic, conjugated or non conjugated dienes, such as 1,4-hexadiene, isoprene, 1,3-butadiene, 1,5-hexadiene and 1,6-heptadiene.

The units deriving from α -olefins of formula $\text{CH}_2=\text{CHR}^{10}$, from cycloolefins and/or from polienes are present in the copolymers preferably in amounts ranging from 1% to 20% by mole.

The saturated elastomeric copolymers can contain ethylene units and α -olefins and/or non conjugated diolefins able to cyclopolymerise. The unsaturated elastomeric copolymers can contain, together with the units deriving from the polymerisation of ethylene and α -olefins, also small proportions of unsaturated units deriving from the copolymerization of one or more polyenes. The content of unsaturated units is preferably comprised between 0 and 5% by weight.

Non limitative examples of suitable α -olefins comprise propylene, 1-butene and 4-methyl-1-pentene. Suitable non conjugated diolefins able to cyclopolymerise comprise 1,5-hexadiene, 1,6-heptadiene and 2-methyl-1,5-hexadiene.

Non limitative examples of suitable polyenes are:

(i) polyenes able to give unsaturated units, such as:

- linear, non-conjugated dienes, such as 1,4-hexadiene trans, 1,4-hexadiene cis, 6-methyl-1,5-heptadiene, 3,7-dimethyl-1,6-octadiene and 11-methyl-1,10-dodecadiene;
- bicyclic diolefins, such as 4,5,8,9-tetrahydroindene and 6 and 7-methyl-4,5,8,9-tetrahydroindene;
- alkenyl or alkyliden norbornenes, such as 5-ethyliden-2-norbornene, 5-isopropyliden-2-norbornene and exo-5-isopropenyl-2-norbornene;
- polycyclic diolefins, such as dicyclopentadiene, tricyclo-[6.2.1.0^{2,7}]4,9-undecadiene and the 4-methyl derivative thereof;

- (ii) non-conjugated diolefins able to cyclopolymerise, such as 1,5-hexadiene, 1,6-heptadiene and 2-methyl-1,5-hexadiene;
- (iii) conjugated dienes, such as butadiene and isoprene.

Another object of the present invention is a process for the polymerisation of propylene carried out in the presence of the above described catalyst.

A further interesting use of the catalysts according to the present invention is for the preparation of cycloolefin polymers. Monocyclic and polycyclic olefin monomers can be either homopolymerised or copolymerised, also with linear olefin monomers.

Polymerisation processes according to the present invention can be carried out in gaseous phase or in liquid phase, optionally in the presence of an inert hydrocarbon solvent either aromatic (such as toluene), or aliphatic (such as propane, hexane, heptane, isobutane and cyclohexane).

The polymerisation temperature is preferably ranging from about 0°C to about 250°C. In particular, in the processes for the preparation of HDPE and LLDPE, it is preferably comprised between 20°C and 150°C and, more preferably between 40°C and 90°C, whereas for the preparation of the elastomeric copolymers it is preferably comprised between 0°C and 200°C and, more preferably between 20°C and 100°C.

The polymerization pressure is ranging from 0,5 to 100 bar, preferably from 2 to 50 bar, and more preferably from 4 to 30 bar.

The molecular weight of the polymers can be also varied merely by varying the polymerization temperature, the type or the concentration of the catalytic components or by using molecular weight regulators such as, for example, hydrogen.

The molecular weight distribution can be varied by using mixtures of different metallocenes, or carrying out the polymerization in several steps at different polymerization temperatures and/or different concentrations of the molecular weight regulator.

The polymerization yields depend on the purity of the metallocene component of the catalyst. Therefore, in order to increase the yields of polymerization, metallocenes are generally used after a purification treatment.

The components of the catalyst can be brought into contact before the polymerization. The pre-contact concentrations are generally between 1 and 10^{-8} mol/l for the metallocene component (A), while they are generally between 10 and 10^{-8} mol/l for the component (B). The pre-contact is generally effected in the presence of a hydrocarbon solvent and, if appropriate, of small quantities of monomer. The pre-contact time is generally comprised between 1 minute and 24 hours.

The following examples are given to illustrate and not to limit the invention.

GENERAL PROCEDURES CHARACTERIZATIONS

All operations were performed under nitrogen by using conventional Schlenk-line techniques. Solvents were distilled from blue Na-benzophenone ketyl (Et_2O), CaH_2 (CH_2Cl_2) or AliBu_3 (hydrocarbons), and stored under nitrogen. BuLi (Aldrich) was used as received.

The $^1\text{H-NMR}$ analyses of the metallocenes were carried out on an AC200 Bruker spectrometer (CD_2Cl_2 , referenced against the middle peak of the triplet of the residual CHDCl_2 at 5.35 ppm). All NMR solvents were dried over P_2O_5 , and distilled before use. Preparation of the samples were carried out under nitrogen using standard inert atmosphere techniques.

The $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ analyses of the polymers were carried out on a Bruker 400 MHz instrument. The samples were analysed as solutions in tetrachlorodideuteroethane at 130°C.

The intrinsic viscosity $[\eta]$ (dl/g) was measured in tetralin at 135°C.

The melting point T_m (°C) and ΔH (J/g) of the polymers were measured by Differential Scanning Calorimetry (DSC) on a Mettler apparatus, according to the following procedure: about 10 mg of sample obtained from the polymerisation were heated to 180°C with a scanning speed equal to 20°C/minute; the sample was kept at 180°C for 5 minutes and thereafter was cooled with a scanning speed equal to 20°C/minute. A second scanning was then carried out according to the same modalities as the first one. The reported values are the ones obtained in the second scanning.

The density (g/ml) was determined by immersion of a sample of extruded copolymer in a column with a density gradient according to the ASTM D-1505 method.

In the copolymers according to the present invention, the product of the reactivity ratios $r_1 r_2$, wherein r_1 is the relative reactivity of the alpha-comonomer versus ethylene and r_2 that of ethylene versus the alpha-comonomer.

PREPARATION OF THE LIGANDS

(N-*t*-butylamino)(dimethyl)(cyclopentadienyl)silane and (N-*t*-butylamino) (dimethyl) (methylcyclopentadienyl) silane were prepared as described in International Patent Application PTC/US92/08730, 1992, in the name of Nickias, P.N., Devore, D.D. Bis(1,3-bistrimethylsilylcyclopentadienyl)zirconium dichloride was purchased from Boulder Scientific Co., Mead Co, USA. Bis(cyclopentadienyl)zirconium dichloride was purchased from Strem Chemicals, Inc., Newburyport, MA, USA.

Example 1

Preparation of 1,1,3,3-tetramethyl-1,2,3,3a-tetrahydrocyclopenta[c] [1,2,5] azadisilole

(N-t-butylamino)(dimethyl)(cyclopentadienyl)silane (0.071 mol, 13.9 g) was dissolved in THF (100 mL) and treated with BuLi (144 mmol of a 2.5 M solution in hexanes) at 0 °C. After stirring for 16 h at room temperature, the dianion solution and a THF solution (75 mL) of dichlorodimethylsilane (0.071 mol) were added dropwise simultaneously to a flask containing 25 mL of THF stirring at -10 °C. The mixture was warmed to room temperature and stirred overnight. Solvents were removed *in vacuo*, and the residue was extracted with pentane. After filtration and evaporation of pentane, the extract was distilled giving 1.2 g of a colorless liquid identified to be 1,1,3,3-tetramethyl-1,2,3,3a- tetrahydrocyclopenta[c] [1,2,5] azadisilole and isomers. ¹H-NMR δ (CDCl₃) (major isomer): 6.7 (m, 3H), 5.7 (broad s, 2H), 1.3 (s, 9H), 0.2 (s, 12H). ms (m/e) (rel intensity): 251 ([PM], 12), 236 (100), 179 (4), 114 (4), 73 (7).

Example 2

Preparation of 1,1,3,3,5-pentamethyl-1,2,3,3a- tetrahydrocyclopenta[c] [1,2,5] azadisilole

(N-t-butylamino)(dimethyl)(methylcyclopentadienyl)silane (0.070 mol, 14.7 g) was dissolved in THF (199 mL) and treated with butyllithium (0.14 mol of a 2.5 M sol. in hexanes) at -78 °C. After stirring for 16 h at room temperature, the dianion solution was added dropwise to a solution of dichlorodimethylsilane (0.070 mol, 9.03 g) in THF (100 mL) at -78 °C. The mixture was slowly warmed to room temperature while stirring overnight. After evaporating the solvent, the residue was extracted with pentane, filtered, and evaporated to an oil. The oil was distilled giving 5.0 g of a colorless liquid identified as 1,1,3,3,5-pentamethyl-1,2,3,3a- tetrahydrocyclopenta[c] [1,2,5] azadisilole and isomers. ¹H-NMR δ (CDCl₃) (major isomer): 6.3 (m, 1H), 5.8 (broad s, 1H), 4.9 (broad s, 1H), 2.1 (s,

3H), 1.3 (s, 9H), 0.3 (broad s, 6H), 0.15 (broad s, 6H). ms (m/e) (rel intensity): 265 ([PM], 14), 250 (100), 193 (3), 135 (4), 73 (16).

Example 3

Preparation of 1,1,5-trimethyl-3-phenyl-1,2,3,3a-tetrahydrocyclopenta[c][1,2,5]azaborasilole

(N-t-butylamino)(dimethyl)(methylcyclopentadienyl)silane (95.7 mmol, 20 g) was dissolved in THF (120 mL) cooled at -78 °C and treated with butyllithium (2.1 eq., 201 mmol of a 2.5 M sol. in hexanes). The solution was stirred for 4 h at room temperature. At -78 °C 95.1 mmol (15.7 g) of PhBCl₂ in 20 ml of pentane were added dropwise. The mixture was slowly warmed to room temperature and stirred overnight. After filtration and evaporating the solvent an orange-oil was obtained. The oil was distilled giving 7.0 g of a colorless liquid identified as the title compound. ms (m/e) (rel intensity): 295 ([PM], 80), 280 (70), 239 (30), 224 (70), 160 (100).

Example 4

Preparation of 1,1,5-trimethyl-3-phenyl-1,2,3,3a-tetrahydrocyclopenta[c] [1,2,5]azaphosphasilole

(N-t-butylamino)(dimethyl)(methylcyclopentadienyl)silane (20 mmol, 4.17 g) was dissolved in THF (25 mL) cooled at -78 °C and treated with butyllithium (40 mmol, 16 ml of a 2.5 M sol. in hexanes). After the reaction was completed the solution was stirred for 1.5 h at room temperature. In a separate 250 ml flask 2.7 ml (20 mmol) of dichlorophenylphosphine and 25 ml THF were added. At -78 °C the above dianion was added dropwise, warmed to room temperature and stirred for 2 h. After filtration and evaporating the solvent 6.61 g of an

orange-oil was obtained. After washing with hexane 3.68 g of a pentane soluble oil was obtained identified as the title compound. ms (m/e) (rel intensity): 315 ([PM], 100), 300 (40), 244 (50), 135 (30), 57 (60).

PREPARATION OF THE METALLOCENES

Example 5

Preparation of Bis(1,1,3,3-tetramethyl-1,2,3-trihydrocyclopentadienyl[c][1,2,5]azadisilole)ZrCl₂

Butyllithium (4.0 mmol of a 2.5 M sol. in hexanes) was added slowly to a solution of 1,1,3,3-tetramethyl-1,2,3,3a-tetrahydrocyclopenta[c] [1,2,5] azadisilole (3.8 mmol, 0.95 g) in ether (30 mL) at -78 °C. The reaction mixture was warmed to room temperature and stirred for an additional 3 h. Solvents were removed *in vacuo* and the residue was mixed with ZrCl₄ (1.9 mmol, 0.443 g) in a glove box. The mixture was slurried in pentane (40 mL)/ether (1 mL) and stirred for 16 h. After evaporating the solvents, the residue was extracted with dichloromethane and filtered. Evaporation of the filtrate gave 1.0 g of bis(1,1,3,3-tetramethyl-1,2,3,3a-tetrahydrocyclopentadienyl[c][1,2,5]azadisilole)ZrCl₂, (1,2(tBuN=(SiMe₂)₂)Cp)₂ZrCl₂. as a tan powder. ¹H-NMR δ (CD₂Cl₂): 6.85 (s, 2H), 6.5 (t, 1H), 1.4 (s, 9H), 0.6 (s, 6H), 0.3 (s, 6H).

POLYMERIZATION OF ETHYLENE

Methylalumoxane (MAO)

A commercial product commercialised by Schering was used in solution of 10% by weight in toluene.

EXAMPLES 6 TO 9

A dry 200 mL glass autoclave equipped with magnetic stirrer, temperature probe, and feed line for ethylene was sparged with ethylene at 35 °C. At room temperature, 90 mL of hexane were introduced. The catalyst system was prepared separately in 10 mL of hexane by consecutively introducing the methylalumoxane, or triisooctylaluminum/water (Al/H₂O = 2.1) mixture, and after 5 minutes stirring, the metallocene compound (1,2(tBuN=(SiMe₂)₂)Cp)₂ZrCl₂ dissolved in minimum amount of toluene. After stirring for 5 minutes, the solution was introduced into the autoclave under ethylene flow, the reactor was closed, the temperature was raised to 80 °C and pressurized with ethylene to 4.6 barg. The total pressure was kept constant by feeding ethylene on demand. The polymerization was stopped by cooling, degassing the reactor, and introducing 1 mL of methanol. The resulting polymer was washed with acidic methanol, methanol, and dried in an oven at 60 °C under vacuum. The results are listed in Table 1. The polymerization conditions are reported in table 1.

Examples 10 to 11 (Comparison)

The examples were repeated according to the procedure described in the examples 6-9, but using bis[1,3-bis(trimethylsilyl) cyclopentadienyl] zirconium dichloride instead of Bis(1,1,3,3-tetramethyl-1,2,3, trihydrocyclopentadienyl[c][1,2,5] azadisilole)ZrCl₂. The polymerization conditions are reported in table 1.

Examples 12 to 13 (Comparison)

The examples were repeated according to the procedure described in the examples 6-9, but using bis(cyclopentadienyl)zirconium dichloride instead of Bis(1,1,3,3-tetramethyl-1,2,3, trihydrocyclopentadienyl[c][1,2,5] azadisilole)ZrCl₂. The polymerization conditions are reported in table 1.

Table 1.
Ethylene polymerization results

Ex.	metallocene, cocatalyst,	Al/Zr	time,	Pol.	Activity	[η],
	mg (μ mol)	(mmol)	mol. ratio	min	g	Kg/gZr/h
6	1.00 (1.51)	MAO (1.51)	1000	10	2.43	105.83
7	0.50 (0.76)	MAO (0.76)	1000	10	2.65	230.83
8	0.16 (0.24)	MAO (0.25)	1026	10	0.84	228.65
9	0.50 (0.76)	TIOA-H ₂ O	1013	8	0.42	45.73
			(0.765)			
10	0.13 (0.22)	MAO (0.23)	1028	15	1.34	262.68
comp.						2.05
11	0.13 (0.22)	TIOA-H ₂ O	1073	20	0.20	29.40
comp.			(0.24)			n.d.
12	0.10 (0.34)	MAO (0.35)	1023	10	1.07	205.76
comp.						2.99
13	0.30 (1.03)	TIOA-H ₂ O	997	20	traces	
comp.			(1.02)			

n.d.=not determined

COPOLYMERISATION OF ETHYLENE WITH 1-HEXENE**Example 14**

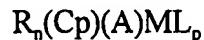
A dry 200 mL glass autoclave equipped with magnetic stirrer, temperature probe, and feed line for ethylene was sparged with ethylene at 35 °C. Heptane (80 mL) and 1-hexene (10 ml) were introduced at room temperature. The catalyst system was prepared separately in 10 mL of heptane by consecutively introducing methylalumoxane (0.33 mmol) and the metallocene (0.2 mg) dissolved in 3 mL of toluene. After stirring for 5 minutes, the solution was introduced into the autoclave under ethylene flow, the reactor was closed, the temperature was raised to 70 °C and pressurized with ethylene to 4.5 barg. The total pressure was kept constant by feeding ethylene on demand. After 10 minutes, the polymerization was stopped by cooling, degassing the reactor, and introducing 1 mL of methanol. The resulting polymer was washed with acidic methanol, methanol, and dried in an oven at 60 °C under vacuum. 1.2 g of polymer were recovered (activity of 261 Kg/g-Zr/h) and a value of $[\eta] = 1.0$ dL/g was obtained, and 7.7 wt.% of 1-hexene was incorporated.

DSC analysis (2° melt); $T_m=114^\circ\text{C}$; $\Delta H=142$ J/g.

The ^{13}C NMR analysis showed the presence of 2.72 mol% 1-hexene content, a n_E (average ethylene sequence lenght) of 37 and value of $r_1=62.1$, $r_2=0.034$, and $r_1xr_2=2.11$.

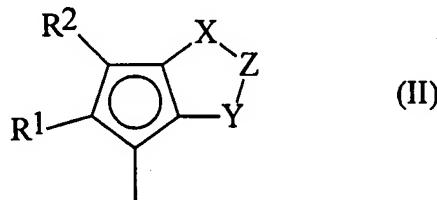
CLAIMS

1. A metallocene compound of formula (I):



wherein R_n is a structural bridge;

Cp is a heterocyclic cyclopentadienyl group of formula (II):



wherein substituents R^1 and R^2 , same or different, are hydrogen atoms, C_1-C_{20} alkyl, C_3-C_{20} cycloalkyl, C_2-C_{20} alkenyl, C_6-C_{20} aryl, C_7-C_{20} alkylaryl, or C_7-C_{20} arylalkyl radicals, optionally two adjacent substituents R^1 and R^2 can form a cycle comprising from 5 to 8 carbon atoms and, furthermore, substituents R^1 and R^2 can contain silicon or germanium atoms;

Z is NR^3 or O , R^3 being defined as substituents R^1 and R^2 ;

X and Y , same or different, are selected from $(CR^4_2)_n$, BR^4_2 , PR^4 , SiR^4_2 or GeR^4_2 ; and substituents R^4 , same or different, are hydrogen atoms, C_1-C_{20} alkyl, C_3-C_{20} cycloalkyl, C_2-C_{20} alkenyl, C_6-C_{20} aryl, C_7-C_{20} alkylaryl or C_7-C_{20} arylalkyl radicals; and, furthermore, substituents R^4 can contain hetero atoms such as nitrogen, phosphor, oxygen, silicon or germanium atoms, with the proviso that both X and Y can not be carbon atoms at the same time;

A is a group selected from substituted or unsubstituted cyclopentadienyls, which may carry one or more condensed cycles, =NR⁵, -O-, -S- and =PR⁵ groups, R⁵ being defined as substituents R¹ and R², and groups corresponding to formula (II);

M is a transition metal selected from those belonging to group 3, 4, 5 or 6 or to the lanthanides or the actinides of the Periodic Table of the Elements (new IUPAC version); the substituent L, same or different, is a monoanionic ligand, selected from the group consisting of hydrogen, halogen, -SR⁶, R⁶, -OR⁶, -NR⁶₂, OCOR⁶, OSO₂CF₃ and PR⁶₂, wherein the substituents R⁶, same or different, are linear or branched, saturated or unsaturated C₁-C₂₀ alkyl, C₃-C₂₀ cycloalkyl, C₂-C₂₀ alkenyl, C₆-C₂₀ aryl, C₇-C₂₀ alkylaryl, or C₇-C₂₀ arylalkyl radicals, optionally containing silicon or germanium atoms;

p is an integer from 0 to 3, p being equal to the oxidation state of the metal M minus two;

n is an integer ranging from 0 to 4; and

r is an integer ranging from 1 to 4.

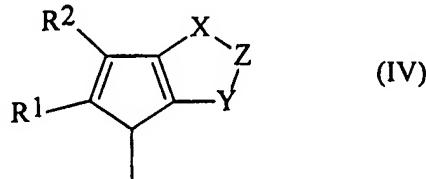
2. The metallocene according to claim 1, characterised in that R is QR⁷_m, Q being C, Si, Ge, N or P, and the R⁷ groups, equal or different, are linear or branched, saturated or unsaturated C₁-C₂₀ alkyl, C₃-C₂₀ cycloalkyl, C₂-C₂₀ alkenyl, C₆-C₂₀ aryl, C₇-C₂₀ alkylaryl, or C₇-C₂₀ arylalkyl radicals optionally, when Q is C, Si or Ge, both substituents R⁷ can form a cycle comprising from 3 to 8 atoms; and
m is 1 or 2, being 1 when Q is N or P, and being 2 when Q is C, Si or Ge.
3. The metallocene according to claim 2, characterised in that (QR⁷_m)_n is selected from the group consisting of CR⁷₂, SiR⁷₂, GeR⁷₂, NR⁷, PR⁷ and (CR⁷₂)₂, R⁷ being defined as in claim 2.

4. The metallocene according to claim 3, characterised in that $(QR^7_m)_n$ is selected from the group consisting of $\text{Si}(\text{CH}_3)_2$, SiPh_2 , CH_2 , $(\text{CH}_2)_2$ and $\text{C}(\text{CH}_3)_2$.
5. The metallocene according to claim 1, wherein the transition metal is selected from titanium, zirconium and hafnium.
6. The metallocene compound according to claim 1, wherein the substituent L is a halogen or a substituent R^6 .
7. The metallocene compound according to claim 1, wherein substituents R^1 and R^2 are hydrogen atoms.
8. The metallocene compound according to claim 1, wherein A corresponds to formula (II), as defined in claim 1.
9. A ligand of formula (III):



wherein R_n is a structural bridge;

Cp is a heterocyclic cyclopentadienyl group of formula (IV):



and its double bond isomers, wherein substituents R^1 and R^2 , same or different, are hydrogen atoms, C_1 - C_{20} alkyl, C_3 - C_{20} cycloalkyl, C_2 - C_{20} alkenyl, C_6 - C_{20} aryl, C_7 - C_{20} alkylaryl, or C_7 - C_{20} arylalkyl radicals, optionally two adjacent substituents R^1 and R^2 can form a cycle comprising from 5 to 8 carbon atoms and, furthermore, substituents R^1 and R^2 can contain silicon or germanium atoms;

Z is NR^3 or O, R^3 being defined as substituents R^1 and R^2 ;

X and Y, same or different, are selected from $(CR^4_2)_r$, BR^4_2 , PR^4 , SiR^4_2 or GeR^4_2 ; and substituents R^4 , same or different, are hydrogen atoms, C_1-C_{20} alkyl, C_3-C_{20} cycloalkyl, C_2-C_{20} alkenyl, C_6-C_{20} aryl, C_7-C_{20} alkylaryl or C_7-C_{20} arylalkyl radicals; and, furthermore, substituents R^4 can contain hetero atoms such as nitrogen, phosphor, oxygen, silicon or germanium atoms, with the proviso that both X and Y can not be carbon atoms at the same time;

A is a group selected from substituted or unsubstituted cyclopentadienyls, which may carry one or more condensed cycles, $=NR^5$, $-O-$, $-S-$ and $=PR^5$ groups, R^5 being defined as substituents R^1 and R^2 , and groups corresponding to formula (IV);

n is an integer ranging from 0 to 4;

q is an integer ranging from 0 to 1; and

r is an integer ranging from 0 to 4.

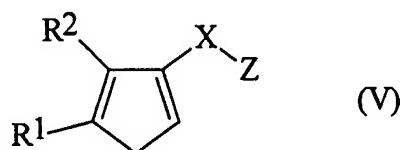
10. The ligand according to claim 9, wherein R is QR^7_m , Q being C, Si, Ge, N or P, and the R^7 groups, equal or different, are linear or branched, saturated or unsaturated C_1-C_{20} alkyl, C_3-C_{20} cycloalkyl, C_2-C_{20} alkenyl, C_6-C_{20} aryl, C_7-C_{20} alkylaryl, or C_7-C_{20} arylalkyl radicals optionally, when Q is C, Si or Ge, both substituents R^7 can form a cycle comprising from 3 to 8 atoms;

m is 1 or 2, being 1 when Q is N or P, and being 2 when Q is C, Si or Ge.

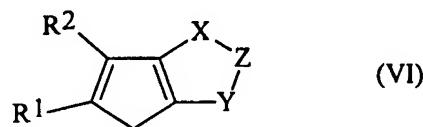
11. The ligand according to claim 10, characterised in that $(QR^7_m)_n$ is selected from the group consisting of CR^7_2 , SiR^7_2 , GeR^7_2 , NR^7 , PR^7 and $(CR^7_2)_2$, R^7 being defined as in claim 1.
12. The ligand according to claim 11, characterised in that $(QR^7_m)_n$ is selected from the group consisting of $Si(CH_3)_2$, $SiPh_2$, CH_2 , $(CH_2)_2$ and $C(CH_3)_2$.
13. The ligand according to claim 9, wherein substituents R^1 and R^2 are hydrogen atoms.

14. The ligand according to claim 9, wherein A corresponds to formula (IV), as defined in claim 9.

15. A process for the preparation of a ligand $R_n(Cp)(A)_q$ of formula (III), Cp and A being defined as in claim 9, and both n and q are 0, comprising the step of contacting a compound of formula (V):



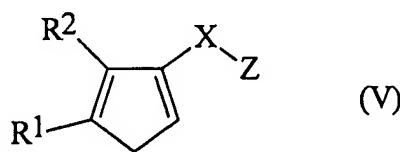
and its double bond isomers, wherein X, R^1 and R^2 are defined as in Claim 9 and Z is nitrogen, with a compound of general formula YZ_2 , wherein Y is defined as in claim 9 and Z' is a halogen atom, in the presence of a base, to form a compound of formula (VI)



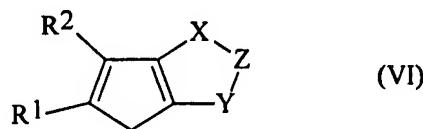
and its double bond isomers.

16. A process for the preparation of a ligand $R_n(Cp)(A')_q$ of formula (IIIa), wherein R is QR^7_m as defined in any of claims 10 to 12, n is an integer from 1 to 4 and q is 1, A' is a group selected from substituted or unsubstituted cyclopentadienyls, which may carry one or more condensed cycles, $=NR^5$, $-O-$, $-S-$ and $=PR^5$ groups, R^5 being defined as substituents R^1 and R^2 , Cp corresponds to formula (IV) and Z' is a halogen atom, comprising the following steps:

(a) contacting a compound of formula (V):

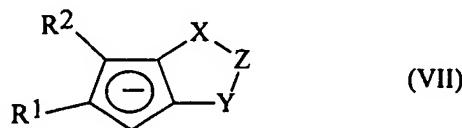


and its double bond isomers, wherein X, R¹ and R² are defined as in Claim 9 and Z is nitrogen, with a compound of general formula YZ'₂, wherein Y is defined as in claim 9 and Z' is a halogen atom, in the presence of a base, to form a compound of formula (VI)



and its double bond isomers, and

(b) contacting with a compound able to form an anion of formula (VII)



and thereafter with a compound of general formula (VIII) R_nZ'₂, in a molar ratio (VII)/(VIII) equal to or higher than 2, or with a compound of general formula (IX) Z'R_nA'HR⁵, in a molar ratio (VII)/(IX) equal to or greater than 1.

17. The process according to claim 15 or 16, wherein both said base to form the compound of formula (VI) and the compound able to form said anion of formula (VII) is selected from the group consisting of hydroxides and hydrides of alkali- and earth-alkali metals, metallic sodium and potassium, and organometallic lithium salts.
18. The process according to claim 17, wherein both said base to form the compound of formula (VI) and the compound able to form said anion of formula (VII) is n-butyllithium.

19. The process according to claim 16, wherein the halogen atom Z' of the general formulae (VIII) and (IX) is a chlorine atom.
20. A process for the preparation of a metallocene compound according to claim 1, obtainable by contacting the ligand $R_n(Cp)(A)_q$ of formula (III) according to claim 9, with a compound capable of forming a corresponding dianionic compound thereof and thereafter with a compound of formula ML_{p+2} , wherein M, L and p are defined as in claim 1.
21. A process for the preparation of a metallocene compound according to claim 20, wherein A corresponds to formula (II).
22. The process according to claim 20, wherein the compound able to form said corresponding dianionic compound is selected from the group consisting of hydroxides and hydrides of alkali- and earth-alkali metals, metallic sodium and potassium, and organometallic lithium salts.
23. The process according to claim 22, wherein the compound able to form said dianionic compound is n-butyllithium.
24. The process according to Claim 20, wherein the compound of formula ML_{p+2} is selected from titaniumtetrachlorid, zirconiumtetrachlorid and hafniumtetrachlorid.
25. A catalyst for the polymerization of olefins, obtainable by contacting:
26. (Q)a metallocene compound of formula (I) according to any of claims 1 to 8, and
27. (R)an alumoxane and/or a compound capable of forming an alkyl metallocene cation.
28. The catalyst according to Claim 25, characterized in that said alumoxane is obtained by contacting water with an organo-aluminium compound of formula AlR^8 , or Al_2R^8 , where at least one R^8 is not halogen.

29. The catalyst according to claim 26, wherein the molar ratio between the aluminium and water is in the range of 1:1 and 100:1.
30. The catalyst according to claim 25, characterized in that said alumoxane is selected from MAO, TIBAO and TIOAO and said organo-aluminium compound is TIOA, TMA and/or TIBA.
31. The catalyst according to claim 25, characterized in that the compound able to form a metallocene alkyl cation is a compound of formula T^+D^- , wherein T^+ is a Brønsted acid, able to give a proton and to react irreversibly with a substituent L of the metallocene of formula (I) and D^- is a compatible anion, which does not coordinate, which is able to stabilize the active catalytic species originating from the reaction of the two compounds, and which is sufficiently liable to be able to be removed from an olefinic substrate.
32. The catalyst according to claim 29, characterized in that the anion D^- comprises one or more boron atoms.
33. A process for the polymerization of olefins, said process comprising the polymerization reaction of one or more olefin monomers in the presence of a catalyst as claimed in any of claims 25 to 30.
34. The process according to claim 31, wherein the olefin monomers are ethylene and/or propylene.

INTERNATIONAL SEARCH REPORT

Int'l. Application No
PCT/EP 99/03247

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C07F17/00 C07F7/08
C07F9/6541

C07F7/30

C07F5/02

C08F10/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C07F C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category ^a	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>SAKURAI, HIDEKI ET AL: "Chemistry of organosilicon compounds. 193. Intramolecular cyclotrimerization of macrocyclic and acyclic triynes with Group 6 metal carbonyls. The formation of fulvene and benzene" J. AM. CHEM. SOC. (1984), 106(26), 8315-16 , 1984, XP002111581 see page 8315, compound 4 ---</p>	1
A	<p>EP 0 590 486 A (IDEMITSU KOSAN COMPANY) 6 April 1994 (1994-04-06) cited in the application claims -----</p>	1,25,33

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

^a Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
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- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the International search

9 August 1999

Date of mailing of the International search report

19/08/1999

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 99/03247

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 590486	A 06-04-1994	JP 6340704 A	13-12-1994